Accurate acoustic measurements in gases under difficult conditions

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(Received 2 May 1991; accepted for publication 20 May 1991)

Accurate measurements of the speed of sound in gases are often made using metal resonators with small transducers that perturb the resonance frequencies in minor and predictable ways. We extend this method to gases that may be corrosive and to high temperatures by using remote transducers coupled to a resonator by acoustic waveguides. Thin metal diaphragms separate the waveguides from the resonator. Thus, only metal parts come into contact with the test gas. In the present apparatus, any gas compatible with gold and stainless steel can be studied.

I. INTRODUCTION

Acoustic resonators have been developed as highly precise and accurate tools for measuring the speed of sound u in gases.[1-9] Moldover *et al.*[8] demonstrated the accuracy attainable with resonance techniques by determining the universal gas constant R with a fractional error of 1.7×10^{-6} using a three-liter spherical resonator. Smaller spherical resonators are routinely used to measure u in a variety of gases near and well below[4,9] room temperature. A fractional precision of 5×10^{-6} in a $u^2(p)$ isotherm is typical, and second virial coefficients and perfect-gas heat capacities can be determined to 0.1% or better.[1-4] All of these measurements have utilized the low-order radially symmetric modes of a spherical cavity because they are non-degenerate and have resonance frequencies that are insensitive to geometric imperfections of the cavity.[10,11] To excite and detect the sound field, small electroacoustic transducers were either embedded in the walls of the resonators or connected to the resonators by very narrow, short ducts: a technique that caused very minor and predictable perturbations to the resonance frequencies.

Recently, two of us (A. R. H. G. and M. R. M.) optimized the design of a resonator system[12] for rapid, accurate measurements of $u^2(p)$ in gases being screened as alternatives to the environmentally unacceptable refrigerants that are now widely used.[13] We discovered that several of the gases of interest were very soluble in the polymer O-rings used in the apparatus, and we suspect that these gases are also soluble in some of the materials used to construct electroacoustic transducers and to insulate wires. The solubility of the gases led to unacceptably long equilibration times following pressure changes. When a gaseous mixture was studied, the differential solubility of various components of the mixture led to uncontrolled changes in the composition of mixture.[14] It became obvious that the potential accuracy of resonance measurements in these gases could not be achieved until techniques were developed to avoid contact between the gases and polymers. Such techniques are the subject of this article and are applicable to accurate speed of sound measurements in corrosive gases and in gases at high temperatures.

II. APPARATUS, MATERIALS, AND PROCEDURES

The heart of the apparatus consists of the resonator (R), electroacoustic transducers ($S=$ source and $D=$ detector), waveguides, and diaphragms as shown schematically in Fig. 1. The temperature controlled fluid bath is shown to emphasize the spatial separation between the resonator and the transducers. The acoustic waveguides are tubes that carry the sound waves between the resonator and the remote transducers. In the prototype illustrated, the gas in the waveguides is ambient air, and it is separated from the test gas in the resonator by thin metal diaphragms whose vibration couples sound between the two gases. For the present measurements, a stainless steel cylindrical resonator, 14 cm long and 6.5 cm inner diameter, was suspended vertically from the lid of the bath and into the thermostatic fluid. Clearly, a spherical resonator outfitted with similar waveguides and diaphragms and housed in a pressure vessel is more desirable, and we are proceeding with that goal in mind.

A schematic representation of a diaphragm assembly and an attached waveguide is shown in Fig. 2. The diaphragm was a stainless steel disk (1 cm in diameter and 25 μm thick) that had been electron beam welded, around the circumference, to a stainless steel flange. Clearance was provided to allow the diaphragm to flex slightly in both directions under differential pressures.

The waveguide was attached to the flange with Stycast 2850 epoxy.[15] This seal was required to prevent leakage of sound; it need not be vacuum tight. A furnace cement would be a satisfactory substitute for epoxy at high temperatures. A gold O-ring sealed the diaphragm assembly to the resonator. The diaphragm was flush with the inner surface of the resonator when the O-ring was fully compressed. Since this O-ring is in contact with the test gas, it must be chemically compatible and vacuum-tight.

Each waveguide consisted of a horn-shaped section tapering out from the diaphragm to a cylindrical extension tube that provided additional spatial separation between the resonator and the transducers. The horns were manufactured by Bruel and Kjaer[15] for use in probe microphones. Each horn was made of thin walled stainless steel and had and outside diameter of 0.33 cm tapering exponentially to 0.12 cm over 15 cm length. Standing waves in

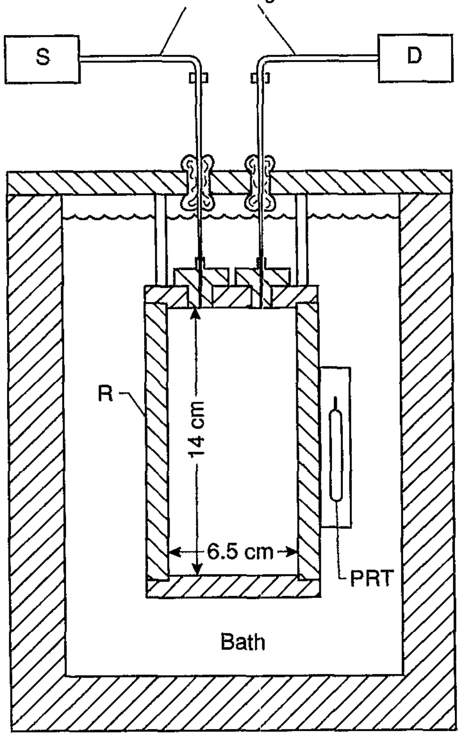

FIG. 1. Sketch of the apparatus, showing the resonator (R) in the temperature controlled environment, the remote source (S) and detector (D) transducers, and the waveguides.

the waveguide are undesirable (because they would couple to the modes of the resonator via the diaphragm) and must be dampened by proper acoustic termination. The horns contain such a termination comprised of a specially designed metal screen mounted in the small diameter end as shown in Fig. 2. The manufacturer's specifications for

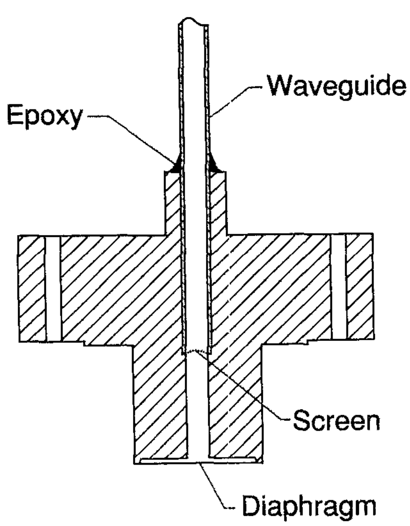

FIG. 2. Cross section through the diaphragm assembly, not to scale. The screen at the end of the waveguide is a resistive acoustic termination to dampen reflections.

these horns shows that the frequency response is flat between 30 and 8000 Hz then drops 20 dB/octave above 10 kHz. The cylindrical extension tubes were stainless steel, 0.32 cm outside diameter with 0.01-cm-thick walls, and about 25 cm long.

Because of the impedance mismatches between the gas in the waveguides, the diaphragms, and the sample gas in the resonator, and because of the screens in the waveguides, the source must deliver higher sound pressure levels than those used in previous apparatuses. We found that a small (approximately 2 cm diameter), commercially available earphone capable of dissipating a few Watts is satisfactory. Its metal diaphragm is able to generate high sound pressure levels into large loads. The source's small size was convenient because it was easily connected to the small diameter waveguide. The detector should also be small and yet sensitive over the entire frequency range of interest (1 to 10 kHz). Knowles Electronics, Inc.[15] makes such a device for use in hearing aids. The device has a built-in preamplifier and a rated sensitivity of 22×10^{-3} V/Pa at 1 kHz. Both transducers were sealed in airtight enclosures and vibrationally isolated from the support structure to reduce the crosstalk between them to an acceptable level.

A stainless steel tube 0.29 cm inside diameter and about 60 cm long (not shown in Fig. 1) was used to admit the sample gas into the resonator. The tube was coiled through the bath to provide good thermal contact. It led from a stainless steel valve at one end to the resonator through a duct. The dimensions of the duct are a compromise between competing requirements. A narrow duct reduces the acoustic energy loss and the undesirable perturbations to the resonator modes, but it results in a low pumping speed for evacuation of the resonator. Kirchhoff–Helmholtz theory[16] predicts the fractional perturbations to the resonance frequencies were less than $\pm15\times10^{-6}$ for the modes we studied, and our measurements on a mock-up confirmed the predictions. The time constant for evacuating the resonator was about 15 min.

Future applications of this new all-metal apparatus may involve conditions under which the sample gas composition could change with time, for example, unstable or reactive gases or at high temperatures. To maintain sample purity under these conditions, it may be necessary to flow the sample gas through the resonator during the speed of sound measurement. No new technology is required to implement this technique; however, an additional exit tube at the opposite end of the resonator and perhaps a port for measuring the static pressure in the resonator will be added.

III. PERFORMANCE TESTS

As a means of characterizing the performance of this all-metal system, we have measured the speed of sound of two gases: argon and CHF_2-O-CHF_2, difluoromethoxydifluoromethane (also known as E134),[17] a proposed alternative refrigerant, between 255 and 373 K. The measurement technique and data analysis will be described in detail in a forthcoming publication. Here, the focus will be on the utility and accuracy of this technique.

The two most important advantages of using diaphragm separators and remote transducers are (1) the removal of elastomers from the environment of the resonator thereby extending its operating temperature range well beyond the limits imposed by these materials and (2) the elimination of contact between elastomers and the test gas. For example, liquid 1,1,-dichloro-2,2,2-trifluoroethane (CCl_2H-CF_3; also called R123) in contact with a Buna-N O-ring for a few hours at room temperature turned brown. The O-ring dramatically increased in size, and its mass increased threefold. A similar test with Viton showed a 50% increase in mass.

The techniques implemented with this new apparatus have eliminated these problems. After an initial vacuum bakeout of the resonator and gas handling system at 383 K to remove water and other volatile contaminants, the outgassing rate was observed to be less than 0.5 Pa per day. During the speed of sound measurements, we left a sample of E134 in the resonator for 10 h at room temperature and a pressure of 120 kPa. Over this time, the pressure changed less than the resolution of the pressure gage (5 Pa) and the fractional change in the speed of sound was within $\pm 4\times 10^{-6}$. At 373 K the speed of sound changed by 10×10^{-6} after 30 h.

The remainder of this article will describe the acoustic performance of the waveguides and diaphragms as measured with this resonator. For a cylindrical cavity, such as our prototype resonator, with radius a and length l, the discrete values of the wave-number k, designated k_{KNS} for the mode (K,N,S), are known functions of a, l, and three non-negative integers K, N, and S (see Ref. 18). The symmetry of each mode is determined solely by (K,N,S): e.g., $(K,0,0)$ refers to purely longitudinal vibrations, $(0,N,0)$ describes vibrations that circulate about the axis of the cylinder, and $(0,0,S)$ designates purely radial vibrations.

We determined the dimensions of the resonator $l(T)$ and $a(T)$ from measurements of the resonance frequencies when the cavity was filled with argon. Argon is an excellent choice because it is chemically inert and because its speed of sound and transport properties are known sufficiently well over a wide range of temperatures and pressures. The viscosity and thermal conductivity are required to calculate the corrections due to the presence of the boundary layer. For the present apparatus, the calibration extends from 255 to 373 K and 8 to 200 kPa.

For a given mode labeled (K,N,S), the speed of sound of the sample gas was determined by measuring the resonance frequency of the mode, correcting for the known perturbations from ideality, and then dividing by $k_{KNS}/2\pi$ as determined from the calibration. The perturbations which we correct for are (1) thermal and viscous boundary layer effects and (2) the fill tube duct. As a measure of systematic errors, we determine the speed of sound of gaseous E134 from several modes using a mode by mode calibration with argon. Figure 3 shows the deviations from the average speed of sound for several modes as a function of pressure at 297 K. For each mode, there

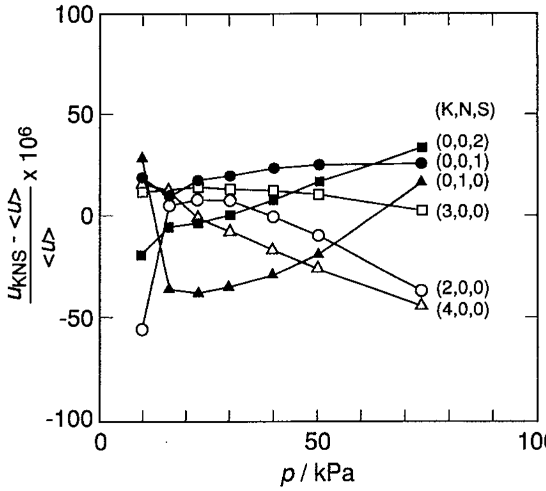

FIG. 3. Deviations of the speed of sound in E134 from the average as a function of pressure for several modes labeled (K,N,S) at 297 K.

are systematic deviations with pressure that have not been removed by the calibration and represent the systematic errors present in the perturbation corrections. However, the maximum spread between the modes of 75×10^{-6} and the fractional standard deviation of 25×10^{-6} are comparable to the errors from the inaccuracy in our knowledge of the transport properties of E134 (15%) and from our limited ability to model the losses in the vicinity of the gold O-rings. For comparison, our previous measurements on E134 using the spherical resonator of Ref. 12 had a maximum spread of 30×10^{-6} between the radial modes and a fractional standard deviation of 8×10^{-6} for a similar isotherm. From these results, we conclude that the diaphragms are not seriously perturbing the resonances over this pressure range.

Although the fractional shift in the resonance frequencies caused by the diaphragms and waveguides is less than 50×10^{-6}, there is a 50–100 fold decrease in the amplitude of the measured resonances as the sample pressure is decreased (increased) from 100 to 10 kPa (200 kPa). Since the pressure in the waveguides was fixed at one atmosphere, the diaphragms were deflected from their no-load positions by the differential pressure across them. When the deflection of a plate is greater than about half the plate thickness, a tension develops and the acoustic transmission is reduced. In this limit the plate begins to act like a membrane under tension. Figure 4 shows the relative transmission through both diaphragms versus the sample pressure. The data points are the scaled resonance amplitude[19] A_{KNS}/Q_{KNS} for three modes with argon and one mode with helium. Q_{KNS} is the quality of the resonance and is the ratio of the resonance frequency to the resonance width at $1/\sqrt{2}$ of the peak amplitude. The solid curve is a model for sound transmission through two diaphragms in a duct, which treats each diaphragm like a membrane with a large static deflection and whose tension is a function of the pressure difference across it.[20–24] An incident acoustic wave induces small oscillations of the diaphragm about its equi-

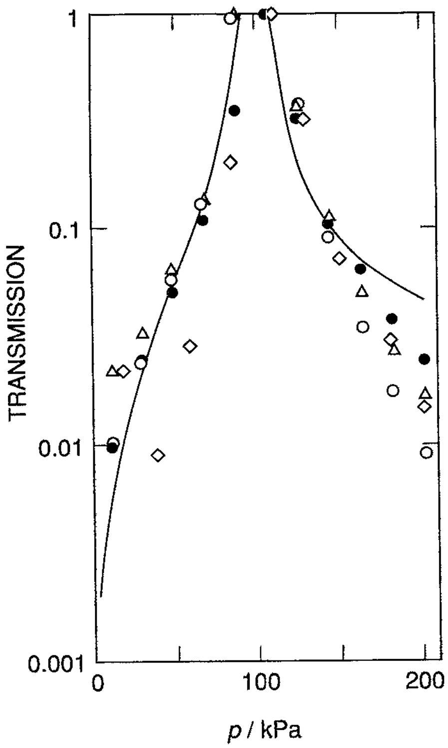

FIG. 4. Relative sound transmission through two diaphragms vs gas pressure p_R in the resonator. The air pressure in the waveguides p_W is constant at 100 kPa. The pressure drop across each diaphragm is $\Delta p = p_W - p_R$. ●: argon at 2280 Hz; △: argon at 4560 Hz; ○: argon at 5970 Hz; ◇: helium at 3590 Hz; —: plate model including membrane forces.

librium position. The transmission through two diaphragms in series is the product of the individual transmission in the large deflection limit. The transmission product is

$$\left|\frac{\delta p_t}{\delta p_i}\right| = \left(\frac{\omega}{3}\right)^2 \left(\frac{1-\nu}{3-\nu}\frac{r^4}{Eh(\Delta p)^2}\right)^{2/3} \rho_R u_R \rho_W u_W, \qquad (1)$$

where the subscripts R and W refer to the gas in the resonator and waveguides, respectively; δp_i and δp_t are the acoustic pressures of the incident and transmitted waves, respectively; ω is the angular frequency; r and h denote the radius and thickness of each diaphragm, respectively; E is Young's modulus and ν is Poisson's ratio for the diaphragm material; $\Delta p = p_W - p_R$ is the pressure difference across each diaphragm; ρ_R and ρ_W are the gas densities; and u_R and u_W are sound speeds of each gas.

Equation (1) shows that the transmission product through two diaphragms varies approximately as $|\Delta p|^{-4/3}$ in the membranelike limit. The small asymmetry about 100 kPa in Fig. 4 is a result of the linear dependence on ρ_R in Eq. (1). If the diaphragms were welded under zero tension, then as $\Delta p \to 0$ the membrane stresses would become negligible compared to the bending stresses (platelike limit), and the transmission would be independent of Δp in this limit.[25] We estimated that if the diaphragms had no wrinkles or buckles when $\Delta p = 0$, this limit would occur when $\Delta p \ll 8E(h/a)^4$ (≈ 1 kPa for these diaphragms). In practice, the presence of buckles in the diaphragms causes this limit to be reached when Δp is approximately 10 kPa; for this reason the comparison in Fig. 4 is meaningful for $|\Delta p| > 10$ kPa.

Understanding the mechanics of the diaphragm transmission under tension is useful for optimizing the trade off between increased acoustic transmission and reduced bursting pressure. Modeling such a diaphragm requires precise knowledge of the boundary conditions at the rim. By sectioning one of the diaphragm housings we observed that the weld would act more like a hinge than a clamp. This condition drastically reduces the bending stresses at the rim that would otherwise occur and increases the bursting pressure. If we assume that rupture occurs when the radial stress equals the tensile strength σ_t of the material (neglecting the effects of fatigue), then the bursting pressure is approximately[26]

$$\Delta p_{\text{burst}} = \frac{8\sigma_t h}{r}\left(\frac{1-\nu}{3-\nu}\frac{\sigma_t}{E}\right)^{1/2}. \qquad (2)$$

Equation (2) is only an estimate of Δp_{burst}, since the actual rupture criterion is very sensitive to the boundary condition at the rim. The bursting pressure for the diaphragms discussed here was estimated to be 715 kPa using $\sigma_t = 620$ MPa, $E = 193$ GPa, $\nu = \frac{1}{3}$, and $r/h = 200$ in Eq. (2). Although Δp_{burst} scales with h/r, Eq. (1) suggests that the transmission scales with $(r^4/h)^{2/3}$, i.e., more can be gained by increasing r than decreasing h. For example, if we increased r by 1.7 times, keeping h the same, we could obtain the same transmission at $\Delta p = 300$ kPa that we measured at 100 kPa with the actual dimensions, and the bursting pressure would decrease to 420 kPa, still 1 atmosphere above the useful pressure range. Of course increasing the diaphragm area also increases the perturbation on the modes of the resonator. Alternatively, the pressure range can be extended by pressurizing the waveguides; however the resistive termination in the waveguides will no longer be optimum and some difficulties with standing waves may occur. We are now studying these effects.

ACKNOWLEDGMENTS

This work was supported in part by the Division of Engineering and Geosciences; Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AI05-88ER13823 and the U.S. Department of the Navy under Interdepartmental Purchase Request N0002490MP33493. We thank Dr. Steve Harsy of W. R. Grace and Co. for providing the purified ether.

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[14] During our earlier measurements (unpublished) on a mixture of E134 and R143 we observed changes in the sound speed of 60 ppm which were uncorrelated with any changes in pressure and attributed them to changes in the gas composition.
[15] In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.
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[19] To determine the transmission through the diaphragms from resonance measurements, we treat the resonator as an amplifier with a gain equal to the quality Q of the resonance. To remove the pressure, frequency, and gas dependence of Q, we scale the resonance amplitude by Q leaving only the response of the diaphragms.
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$$(\partial\zeta_0/\partial p)_{\Delta p} = 3r^4(1-\nu^2)/16Eh^3$$

independent of Δp.
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